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(71) Applicant: COMMONWEALTH OF AUSTRALIA
DEPARTMENT OF INDUSTRY TECHNOLOGY AND COMMERCE
59-61 Goulburn Street
Sydney New South Wales 2000(AU)

(72) Inventor: Akerman, Alfred M.
1302 White Avenue
Knoxville Tennessee 37916(US)

(72) Inventor: Klick, David I.
1060 Greenhills Drive
Ann Arbor Michigan 48105(US)

(72) Inventor: Maynick, Robert George
54 Gould Avenue
St Ives New South Wales 2075(AU)

(72) Inventor: Paul, George Lange
21A Greville Street
Chatswood New South Wales 2067(AU)

(72) Inventor: Reid, Gavin Pierce
3 Gnarvot Avenue
Carss Park New South Wales 2221(AU)

(72) Inventor: Supurovic, Darko
94 Arthur Street
Homebush New South Wales 2140(AU)

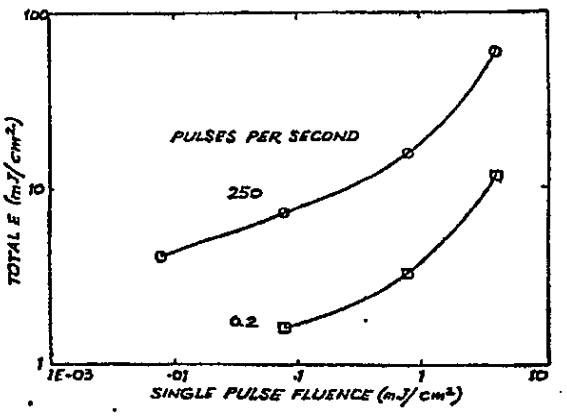
(72) Inventor: Tsuda, Haruki
29 Bannockburn Street
Pymble New South Wales 2073(AU)

(74) Representative: Mair, Richard Douglas et al,
F.J. Cleveland & Company 40-43 Chancery Lane
London WC2A 1JQ(GB)

(54) Laser curing of coatings and inks.

(57) A method of curing polymer coatings by laser photochemistry in which UV laser irradiation of the coating containing a photoinitiator sensitive to a selected wavelength of the laser light effects a low energy cure of the coatings. The total energy to effect a cure is markedly reduced by applying a series of pulses of the laser light at a low single pulse fluence. A reduction of the single pulse fluence at a constant pulse repetition rate or a reduction of the pulse repetition rate at a constant single pulse fluence tends to further reduce the total energy required to effect a cure of the coating.

FIG. 4



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LASER CURING OF COATINGS AND INKS

Th present invention relates to the curing of coatings and inks, and more particularly to laser curing of such coatings and inks.

Clear and pigmented coatings and inks as employed in, say, the printing and painting industries which are susceptible to ultraviolet curing are gaining more acceptance as they can be rapidly cured, require small space for curing, and minimize or eliminate the solvent emitted to the environment. Ultraviolet coatings are typically composed of a liquid or solid polymer and/or oligomer and/or a monomer, and a photoinitiator. A hydrogen donor such as amines or thiols and their analogues including polymeric analogues are optionally included with the photoinitiator to increase production of radicals used to start the polymer chains. When a photoinitiator molecule absorbs a photon of light it can form a radical that combines with a monomer or polymer to start the growth of long chain polymers thereby effecting a cure of the coating or ink. Typical ultraviolet lamp based systems require a fluence of one Joule per square centimetre or greater to ensure cured coatings or films of practical thickness. While the expenditure of such energies leads to practical curing speeds, major advantages are to be gained if the fluence can be reduced so as to allow curing of more film with the same light energy resulting in increased output. Freedom to select the one best wavelength and wavelength bandwidth is also advantageous. Further, when making a thick coating, the surface often cures before the body of the coating, leading to a wrinkling of that coating and poor surface adhesion.

At present ovens are used to remove solvents and thus dry and/or polymerise conventional solvent or aqueous based coatings. Such ovens occupy considerable space and require relatively large amounts of energy to maintain their temperature as well as the provision of ventilation for the

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removal of solvent fumes. The desirability of a more even cure rate through the depth of the coating is readily apparent as are the benefits to be gained by reduced fluence to effect photo-polymerization. At present, UV lamps are used for clear coatings and inks, but ozone, heat removal and non-useful wavelengths of light can reduce their effectiveness. So little light from these lamps can penetrate a typical thick pigmented coating that they are not used commercially to any significant extent for this purpose.

The present invention proposes to ameliorate the problems associated with prior art systems for curing coatings and inks by the use of ultraviolet laser energy specifically selected to effect the cure of predetermined forms of coatings and inks.

In one aspect the present invention consists in a method of curing a coating comprising applying said coating to a surface, said coating comprising a liquid or solid polymer and/or oligomer, and/or a monomer and at least one photoinitiator, and irradiating said coating with ultraviolet laser light of at least one predetermined wavelength, wherein the at least one predetermined wavelength is selected so as to be preferentially absorbed by the at least one photoinitiator rather than the other components of the coating. Where the coating is in the form of a pigmented coating or ink, the coating further comprises a pigment and the at least one predetermined wavelength of said laser light is selected so as to be minimally absorbed by the pigment.

A particularly preferred method in accordance with the invention provides that the laser light is applied to the coating by being pulsed. In a further embodiment at least 25 pulses of the laser light are required to effect a cure. In another

arrangement at least 50 pulses are required to effect a cure. Desirably, the single pulse fluence of the applied laser light is kept low and preferably $\leq$ 3mJ/cm^2. Advantageously, it has been found that the total energy to effect a cure is very significantly reduced where the single pulse fluence is reduced and the total number of pulses applied to the coating or ink is increased while operating at a predetermined pulse repetition rate.

A further embodiment employs two photoinitiators such that each of the two photoinitiators preferentially absorbs a different predetermined wavelength of the laser light so that one photoinitiator is selected for effecting a cure through the coating and the other photoinitiator is selected for effecting a cure at the surface of the coating.

Typically, pigmented coatings are of a thickness $\geq$ 0.5 microns; clear coatings have a thickness $\geq$ 2 microns; and printing inks have a thickness $\leq$ 20 microns.

The laser curing process of the present invention requires little or no solvent to be employed in the coatihg or ink thereby requiring a minimum of space and providing an environmentally acceptable process. Further, the cost of laser curing by the process of the present invention is a fraction of the cost of existing thermal processes and avoids problems associated with air drying. Typical oven drying of pigmented coating requires considerable space and energy to maintain set temperatures, and ventilation facilities to remove the solvent fumes.

By means of the present invention pulses of laser light with fluences as low as 0.0001 millijoule/cm^2/pulse may be used to cure clear polymer coatings. A preferred fluence being 0.002 millijoule/cm^2/pulse and with an application of 180 pulses. With this fluence, a 100 watt UV laser can cure a

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1 metre wide film 7 microns thick, moving at a speed of 750 metres^2/minute. This may be compared with typical speeds of 80 metres^2/minute for single UV lamp curing (200-300 watt/inch lamp intensity over a 1 metre width) and typical speeds of 400 metres^2/minute for single electron beam curing. By means of low single pulse fluence and multiple pulses an extremely energy efficient through cure of a clear polymer coating can be effected. For low fluence curing one may use Beer's law to select the optimum concentration of the photoinitiator for the coating thickness desired in order to arrive at a cure throughout the thickness of the coating. By means of this invention no more light than is required by the photoinitiator need be used as preferentially no other component of the coating would appreciably absorb at the selected wavelength. This process leads to a markedly lower fluence than is typically used in the cure of coatings and although the cost per photon is higher with a laser than with a lamp, the nett cost of effecting a cure is much lower since so many fewer photons are required to that end. As well the lower fluence required to effect a cure translates to a substantially higher throughput of coated material to be cured than heretofore.

In addition the laser source may be placed remote from the coating location since its light output is easily transmitted long distances. Techniques for expanding the beam and making it sufficiently uniform are readily apparent.

In the case of pigmented coatings the present invention has been employed in the curing of commercial quality coatings of 20 microns and larger thicknesses with 50% of rutile TiO_2 by weight. In this example laser light is used to achieve a through cure of the coating by penetrating the coating at a wavelength of minimum absorption due to the pigment. A photoinitiator is used

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that absorbs light at this wavelength and whose concentration may be adjusted for maximum energy efficiency.

Advantageously, a nitrogen atmosphere is used to counteract oxygen inhibition during the curing process and very short pulses of light, typically of the order of 20-40 nonoseconds, are employed to initiate polymer growth in a particular area of the coating. The use of consecutive pulses of short duration promotes the cure to completion in combination with low fluence of light. It has been found that use of laser light in accordance with the present invention, at 50% TiO_2 percent volume concentration has led to a comparable cure with 3 mJ/cm^2 as compared with 16 J/cm^2 using a mercury H lamp and the use of the laser allows room temperature curing. This would mean a 100W laser could support a one metre wide belt moving at 50 metres/min. Other pigments with absorption at shorter wavelengths in the UV region of the spectrum or in thinner coatings, such as inks, would require less energy/cm^2 to cure.

Examples of components employed in typical coatings suitable for curing by the present invention are as follows.

Clear Coatings

Typical UV laser curable coatings suitable for use in the present invention may be composed of but not limited to the following materials:-

1. Reactive Oligomer(s) - A low molecular weight polymer (typically greater than 500 in weight average molecular weight) with one or more reactive functionalities to include unsaturated reaction sites, such as but not limited to acrylates or acrylamides or polyester, polyether, alkyd, cellulosics, acrylic, epoxy, silicone polyester, urethanes or any combination thereof. A polyene/polythiol type system, or a system such as a

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cationic initiated type may also be employed. Anionic initiated types may also be employed.

2. Reactive Diluent(s) - This component could be mono, di, tri, or polyfunctional and typically would also be a low molecular weight product. (Typically 50-500 in weight average molecular weight.)

3. A photoinitiator system(s) - This component will use the incident light to induce radical or ion formation,

4. Optionally an amine or derivative including amino acrylates, and

5. Various additives - These are normally used in conventional paint manufacture, for example, flow modifiers.

6. Optionally solvent or water.

A typical photoinitiator system could preferably include two of the following family groups, as follows:

1. Alkyl benzoin ethers - as an example, Benzoin Butyl Ether marketed as EB3 by Fratelli Lamaberti.

2. Alpha - Acyl oxime esters-1-phenyl-1,2-propanedione-2-(-O-ethoxycarboxyl)oxime, as an example, Quantacure PDC by Ward-Blankensop.

3. Benzimidazoles and azines-2-chloromethyl benzimidazoles.

4. Benzophenones and derivatives - Benzophenone, p-phenyl benzophenone, for example, Trigonal 12 by Akzo Chemie.

5. Acetophenone and derivatives - (alpha,alpha-diethoxyacetophenone) such as DEAP from Upjohn or 2,2-dimethyl-2-phenylacetophenone such as Irgacure 651 from Ciba-Geigy, or 2,2-dimethyl-2-hydroxyacetophenone, such as D1173 from Merck.

6. Hydrogen donors such as amines or thiols and their analogues including polymeric and unstaurated analogues, for example - methyl diethanolamine.

7. Ketones - Michler's Ketone, not normally used due to possible carcinogenic properties, and Darocure 1664 from

Merck.

8. Benzil Ketals - Benzyl dimethyl Ketal, for example KB1 and KB60 from Fratelli-Lamberti.

9. Others not fitting into categories above - 2-methyl-1-(4-methylthiophenyl)-2-morpholinipropanone-1 from Ciba-Geigy, and 1-Benzoyl cyclohexanol from Ciba-Geigy; Acylphosphine oxide and analogues

10. Thioxanthones - These would include the following:

2 and 4-chlorothioxanthone for example CTX by Sherwin Williams.

2,4-diethylthioxanthone, for example DETX

Isopropylthioxanthone, for example ITX

2,4-dimethylthioxanthone, for example RTX.

CTX/MDEOA, DETX/MDEOA, ITX/MDEOA, and RTX/MDEOA. MDEOA may be replaced by Ethyl-p-dimethylaminobenzoate, EPB, and also p-dimethylaminoethylbenzoate. Also relevant, amongst others, are DETX analogues, related polymers and amines and aminobenzoates

Pigmented coatings

Typical UV curable coatings for use in the present invention may typically be composed of the materials recited above for clear coating but together with coloured pigments such as TiO_2. The photoinitiator for titanium dioxide pigment systems typically being CTX/MDEOA, DETX/MDEOA, ITX/MDEOA, and RTX/MDEOA. MDEOA may be replaced by Ethyl-p-dimethylaminobenzoate, EPB, and also p-dimethylaminoethylbenzoate. Also relevant, amongst others, are DETX analogues, and Acyl Phosphine oxide and analogues, related polymers and amines and aminobenzoates.

In the case of pigmented coatings the photoinitiator concentration may be adjusted to minimise the laser energy per sq. cm at a given concentration of pigment which is required to completely cure the coating. Lasers employed in the practice of the invention may typically have a band width of around 5 nanometers or less centred at the

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processing wavelength. There is a narrow optimum in wavelength for each combination of pigment and photoinitiator. Doubling the wavelength spread or shifting the wavelength 5 nanometres either side of optimum will increase the energy requirement.

It has been found that the use of acylphosphine oxide as the photoinitiator is particularly advantageous and its use results in a hard, well cured coating with good and pure white colour. Wavelengths of UV laser between 400 and 450 nm have been successfully employed as rutile TiO_2 does not absorb as strongly in that range. As stated previously, other pigments with absorption at shorter wavelengths in the UV region of the spectrum or thinner coatings, such as inks, will require less energy/cm^2 to cure.The corollary is that photoinitiators are preferred where they absorb at those wavelengths where the pigments used have least absorption.

Benefits and advantages of the application of the present invention will now be described with reference to the accompanying drawings, in which:-

Fig. 1 is a graph demonstrating the comparison between a laser cure in accordance with the present invention and that as possible with a conventional mercury lamp for a particular photoinitiator;

Fig. 2 is a graph of energy to cure a clear coating compared with changes in photoinitiator concentration for two different thicknesses of coating;

Fig. 3 is a graph of energy to cure a clear coating compared with single pulse fluence to achieve that cure with pulses applied at a rate of 250 per second;

Fig. 4 is a graph of energy to cure a clear coating compared with single pulse fluence at two different pulse repetition rates;

Fig. 5 is a graph of transmission spectra of TiO_2 in a pigmented coating for two different concentrations of

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TiO_2;

Fig. 6 is a graph of energy to cure a pigmented coating compared with laser wav length to effect that cure;

Fig. 7 is a graph of energy to cure for a pigmented coating compared with laser wavelength wherein the photoinitiator differs from that of Fig. 6;

Fig. 8 is a graph showing how changes in concentration of two solvents in a dye laser can effect changes in the laser wavelength;

Fig. 9 is a graph of energy to cure a pigmented coating compared with the thickness of the coating for two different pigment concentrations;

Fig. 10 is a graph of energy to cure a pigmented coating compared with single pulse fluence with pulses applied at a rate of 250 per second;

Fig. 11 is a graph of energy to cure a pigmented coating compared with laser pulse repetition rate at a constant wavelength; and

Fig. 12 is a graph of optimum concentration of a photoinitiator compared with illumination intensity of the laser for effecting a cure of a pigmented coating.

Lasers which are typically suited in the operation of the present invention are rare gas halide (excimer) lasers which have achieved marked improvements in reliability and average power since their development in 1976. Lasers of interest include such as are referenced in "Solvent Dependent Characteristics of XeCl Pumped UV Dye Lasers" by Cassard, Corkum and Alcock, Appl. Phys. 25,17-22 (1981).

The basic principle of laser curing of coatings and inks in accordance with the invention relies on the fact that laser light is substantially monochromatic, so that all the light can be employed to perform useful work. The photoinitiator is chosen to have its maximum activity at the laser wavelength. In Fig. 1 the absorption curve of the photoinitiator trigonal 12 is plotted, with the line

showing 100% of the laser light at 308 nm. In contrast, the mercury lamps that are currently used for curing clear coatings have many lines, only a few of which do useful work. For instance, in Fig. 1, emissions of wavelengths above 350 nm are poorly absorbed by the photoinitiator, and emissions below 270 nm do not penetrate the bulk of the coating. The remaining emissions around 300 nm comprise only 10% of the lamp's output light in the UV region.

Fig. 2 demonstrates that very thick (50 - 150 microns) clear coatings may be cured by the laser method. Total laser energy required to cure reaches an optimum for a given concentration of the photoinitiator, DETX. Here and in the following figures, coatings were illuminated by an expanded laser beam in a nitrogen atmosphere until an excellent (commercially acceptable) cure was obtained.

The graph of Fig. 3 shows that a lower fluence (a more expanded laser beam) leads to a lower energy requirement for cure. The lowest fluence allowable is given by the largest practical area of illumination. This in turn determines the lowest possible total fluence and hence the fastest "belt speed" at which material may be cured. The slope of these data is well explained by the theory of radical recombination.

Fig. 4 demonstrates that at a given single pulse fluence, one finds that going to higher pulse repetition rate degrades performance. By going to lower single pulse fluence, some of this loss may be recovered. For maximum belt speed, the laser is run at its maximum repetition rate.

Fig. 5 demonstrates that ultraviolet curing of coatings containing TiO_2 (i.e. opaque paints) must be done at longer wavelength than the absorption edge of TiO_2 (shown here at 400 to 410 nm). At shorter wavelength, the light is all absorbed before reaching the

bottom of the coating.

The theoretical curing speed can be considered to be proportional to the intensity of light reaching the bottom of the coating.

The experimental curve of Fig. 6 for the energy to cure vs. wavelength shows a very sharp optimum for the photoinitiator DETX. The illuminating wavelength should preferably be 422 ± 5 nm. There was 50% Rutile in a 20 micron coating, providing a sufficiently opaque paint for commercial use.

Fig. 7 shows that for another photoinitiator, Acylphosphine oxide, a similarly narrow curing range is found, 413 ± 3 nm. At the present time only a dye laser has the narrowband, tunable radiation needed to cure these pigmented coatings. The dye laser output was measured for Popop dye in cyclohexane/dioxane.

Using various solvents, the dye Popop can be made to lase at many wavelengths (see Fig. 8), including the optimum ones for DETX and acylphosphine oxide (APO) pigmented coatings with TiO_2.

Using different dyes, the dye laser can be made to lase from 330 to 1000 nm with about 25 watts of power (assuming an input beam of 100 watts at 308 nm).

Fig. 9 demonstrates that the dye laser method is able to cure thick (up to 60 microns) pigmented coatings, with different loadings of TiO_2.

As with clear coatings, going to lower intensity illumination of pigmented coatings gives a faster cure rate (less total energy to cure and more efficient use of light). In the plot of Fig. 10 two laser wavelengths were used, 308 and 415 nm. The 308 nm light increases the rate of surface cure.

As shown by Fig. 11 higher repetition rates of the laser lead to less efficient cure for pigmented coatings (as with clear ones).

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The optimum photoinitiator, e.g., acylphosphine oxide, concentration changes with illumination intensity as shown in the plot of Fig. 12. Fortunately, low fluence is associated with both faster cure speeds and lower photoinitiator concentration, which means lower costs.

Examples of cures achieved by operating in accordance with the invention will now be described in relation to inks, clear coatings and pigmented coatings.

Inks

Inks employed in these examples carry the trade name "Viodri" as marketed by Coates Brothers Australia Pty. Ltd., their exact composition is unknown. However, Coates literature says they contain polyfunctional acrylate esters and photoinitiators such as benzophenone.

The inks were spread with a rubber printer's roller onto paperboard to a thickness estimated at 3-5 microns. They were cured quickly so as to reduce soaking into the paper. Curing took place under a nitrogen atmosphere and illumination by excimer laser light at 308 nm, 250 pulses per second for red and yellow inks and 415nm for black and blue inks, and a single pulse fluence of 1 mJ/cm^2. A scratch test was used to determine a successful cure, and the minimum total energy to cure was noted.

Examples:

(Coates ink type - total energy to cure in mJ/cm^2)

1) LUV 308 red - 18
2) LUV 307 yellow - 25
3) LUV 309 blue - 160
4) LUV 311 black - 350

Clear Coatings or Varnishes

Clear varnishes in these examples consisted of epoxy acrylate and HDDA (hexanedioldiacrylate) in a 60/40 ratio. Into this base was mixed a photoinitiator at a .5-3% level, along with an amine (N-methyldiethanol amine) in the same concentration as the photoinitiator. Coatings

were spread onto paperboard with a wire-wound bar for less than 50 micron thickness, or between layers of tape for the 150 micron thickness. Coatings were cured under a nitrogen atmosphere with low fluence illumination directly from an excimer laser operating at 308 nm (Lambda Physik EMG 203) or 351 nm (Lambda Physik 150 ETS). A scratch test was used to determine a successful cure, and the minimum total energy to cure was noted.

1) Very thick layer

Photoinitiator - DETX at concentration 0.5%. Thickness - 150 microns. Single pulse fluence - 1.3 mJ/cm^2. Laser wavelength - 351 nm. Repetition rate - 1 pulse per second. Minimum total energy to cure - 20 mJ/cm^2.

2) Thick Layer

Photoinitiator - Irgacure 651 at concentration 5%. Thickness - 35 microns. Single pulse fluence - 0.008 mJ/cm^2. Laser wavelength - 308 nm. Repetition rate - 250 pulses per second. Minimum total energy to cure - 4 mJ/cm^2.

3) Thin Layer

Photoinitiator - Trigonal 12 at concentration 3%. Thickness - 7 microns. Single pulse fluence - 0.0023 mJ/cm^2. Laser wavelength - 308 nm. Repetition rate - 250 pulses per second. Minimum total energy to cure - 0.41 mJ/cm^2. For a 100 watt laser, this can be extrapolated to a belt speed of 1460 square meters/min for a thin clear coating.

4) Thick Layer

Photoinitiator - Trigonal 12 at concentration 0.75%. Thickness - 35 microns. Single pulse fluence - 0.0008 mJ/cm^2. Laser wavelength - 308 nm. Repetition rate - 250 pulses per second. Minimum total energy to cure - 2 mJ/cm^2. For this 100 watt laser, this result can be extrapolated to a belt speed of 300 square meters/min for

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a thick clear coating.

White Paints

Paints in these examples consisted of the same formulation as the clear varnish (see above), with the addition of a pigment or hiding agent (always rutile TiO_2 particles milled into the varnish). These paints were spread as with the clear varnishes above onto paperboard or primed zincalume metal plates and cured under nitrogen. To minimize absorption in the TiO_2, laser illumination was from a dye laser pumped by the excimer laser at 308 nm, and emitting at 410-430 nm. A scratch test was used to determine a successful cure, and the minimum total energy to cure was noted.

1) Very thick layer on paper

Photoinitiator - acylphosphine oxide at concentration 3%. Thickness - 60 microns. Pigment loading - 32% TiO_2 by weight. Single pulse fluence - 0.023 mJ/cm^2. Laser wavelength - 414.5 nm. Repetition rate - 250 pulses per second. Minimum total energy to cure - 35 mJ/cm^2.

2) Thick layer on paper

Photoinitiator - DETX at concentration 2%. Thickness - 20 microns. Pigment loading - 50% TiO_2 by weight. Single pulse fluence - 0.05 mJ/cm^2. Laser wavelength - 422 nm. Repetition rate - 250 pulses per second. Minimum total energy to cure - 27 mJ/cm^2.

3) Thick layer on paper

Photoinitiator - acylphosphine oxide at concentration 4% and Trigonal 12 at concentration 3%. Thickness - 35 microns. Pigment loading - 32% TiO_2 by weight. Dual wavelength cure: 308 nm at 0.0015 mJ/cm^2 and 415 nm at 0.003 mJ/cm^2. Repetition rate - 250 pulses per second. Minimum total dye laser energy to cure - 2.6 mJ/cm^2. Using the present 25% efficient dye laser, this corresponds to a belt speed of 50 square meters/min for a thick pigmented coating.

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4) Thick layer on metal

Photoinitiator - acylphosphine oxide at concentration 2% and Trigonal 12 at concentration 2%. Thickness - 28 microns. Pigment loading - 32% TiO_2 by weight. Dual wavelength cure: 308 nm at 1.39 mJ/cm^2 and 414.5 nm at 0.03 mJ/cm^2. Repetition rate - 250 pulses per second. Minimum total dye laser energy to cure - 30 mJ/cm^2. Using the present 25% efficient dye laser, this corresponds to a belt speed of 50 square meters/min for a thick pigmented coating.

Examples of formulations of coatings and their manner of application and curing will now be described.

Example I

A typical mix of ingredients for a clear coating in accordance with the invention comprises the following by weight: 56.4% epoxy acrylate oligomer (51-650 of A.C. Hatrick Chemicals Pty. Limited (A.C.H.)); 37.6% H.D.O.D.A. hexane diol diacrylate (A.C.H.); 3% Trigonal 12 phenyl benzophenone (AKZO Chemicals); and 3% MDEOA methyl diethanol amine (Union Carbide).

This mixture was applied wet to a thickness of 7 m by draw down bars and was cured under a nitrogen blanket with a single pulse fluence of 0.0065 millijoules/cm^2. The total energy required to cure was 0.9 mJ/cm^2 and the state of cure was assessed by measuring hardness of the coating via a scratch test.

The substrate to which the coating was applied was high quality low porosity white paper. The wet sample coating having dimensions of 10cm x 5cm was irradiated by a laser beam of dimensions 15cm x 15cm. The results of this static test when extrapolated to a dynamic environment equate to a belt travelling at 667 metres/min, the belt being 1 metre wide and the illuminated area being 1 x $3m^2$.

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Example II

This example also concerns a clear coating formed from the following ingredients in percentages of the total mixture by weight: 56.4% Celrad 3700 epoxy acrylate oligomer (Celanese Corporation); 37.6% HDODA (A.C.H.); 3% Trigonal 12 (AKZO Chemicals); and 3% MDEOA (Union Carbide). The wet coating was applied to a thickness of 5μm with a draw down bar and the same substrate was employed as for Example I but the single pulse fluence applied was 0.00015 millijoules/cm^2 and the total energy to cure was 0.29 mJ/cm^2. The equivalent belt speed in this case is 2069 m/min for the same area of illumination as in Example I.

Example III

A pigmented coating was produced by curing a mixture of the following ingredients combined in weight percentages as follows: 61% of a 60/40 mixture of epoxy acrylate oligomer (ACH 51-650) and H.D.O.D.A. (A.C.H.); 32% TiO_2 RHD_2 (I.C.I); 3% Trigcnal 12; and 4% acyl phosphene oxide (BASF).

The same application conditions were employed as for Examples I and II to a wet thickness of coating of 35 m. Two wavelengths of radiation were employed, the first being 308nm at a single pulse fluence of 0.0015 mJ/cm^2 and the second being 415 nm at a single pulse fluence of 0.0025 mJ/cm^2. The total energy to cure was 1.4mJ/cm^2 for the 308 nm radiation and 2.6 mJ/cm^2 for the 415 nm radiation.

The equivalent belt speed in this case using an illuminated area of 1 x $3m^2$ is 50 m/min.

The advantages flowing from the application of the present invention will be apparent to the addressee and in the case of pigmented coatings, not to mention clear coatings, there is the application of coatings on paper, timber, furniture, metal cans, flat metal plates, steel

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and aluminium coil, interior and exterior of automobiles, component parts, plastic parts tc.

CLAIMS:

1. A method of curing a coating comprising applying said coating to a surface, said coating comprising a liquid or solid polymer and/or oligomer, and/or a monomer and at least one photoinitiator, and irradiating said coating with ultraviolet laser light of at least one predetermined wavelength, wherein the light energy at the at least one predetermined wavelength is selected so as to be preferentially absorbed by the at least one photoinitiator rather than the other components of the coating.

2. A method as claimed in claim 1 wherein at least one predetermined wavelength is a peak wavelength.

3. A method as claimed in claim 1 or 2 wherein the laser light at said at least one predetermined wavelength is applied to the coating by being pulsed.

4. A method as claimed in claim 3 wherein at least 25 pulses are required to effect a cure.

5. A method as claimed in claim 3 wherein at least 50 pulses are required to effect a cure.

6. A method as claimed in any one of claims 3 to 5 wherein the single pulse fluence is less than $3mJ/cm^2$.

7. A method as claimed in any one of claims 3 to 5 wherein the single pulse fluence is less than $1mJ/cm^2$.

8. A method as claimed in any one of claims 3 to 5 wherein the single pulse fluence is less than $0.5\ mJ/cm^2$.

9. A method as claimed in any one of claims 3 to 8 wherein the pulse repetition rate is low.

10. A method as claimed in claim 9 wherein the pulse repetition rate is 250 Hz or less.

11. A method as claimed in any one of claims 3 to 10 wherein a reduction of the single pulse fluence at a constant pulse repetition rate reduces the total energy required to cure said coating.

12. A method as claimed in any one of claims 3 to 10 wherein a reduction of the pulse repetition rate at a

constant single pulse fluence reduces the total energy required to cure said coating.

13. A method of curing a coating as claimed in any one of the preceding claims wherein said coating comprises a pigment and the at least one predetermined wavelength of said laser light is selected so as to be minimally absorbed by said pigment.

14. A method of curing a coating as claimed in claim 13 wherein the coating is in the form of an ink having a thickness $\leq$ 20 microns.

15. A method as claimed in claim 13 wherein the coating has a thickness $\geq$ 0.5 microns.

16. A method as claimed in any one of claims 1 to 12 wherein the coating is a clear coating having a thickness $\geq$ 2 microns.

17. A method as claimed in claim 15 or 16 wherein the coating thickness is $\geq$ 20 microns.

18. A method as claimed in claim 17 when not appended to any one of claims 1 and 2 or 5 to 8 wherein the single pulse fluence is less than $8mJ/cm^2$.

19. A method as claimed in any one of the preceding claims wherein the coating comprises at least two photoinitiators.

20. A method as claimed in claim 19 wherein a first photoinitiator preferentially absorbs a first wavelength of the laser light and the second photoinitiator preferentially absorbs a second wavelength of the laser light such that said one photoinitiator is selected for effecting a cure through the coating and the second photoinitiator is selected for effecting a cure at the surface of the coating.

21. A method as claimed in claim 13 or claim 19 or 20 when appended to claim 11 wherein the pigment is TiO_2.

22. A method as claimed in any one of the preceding claims wherein the curing is conducted under a nitrogen

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atmosphere.

23. A method as claimed in any one of the preceding claims wher in cons cutive, very short duration pulses of said laser light are employed to effect curing.

24. A method as claimed in claim 16, wherein said coating comprises, by weight, 56.4% epoxy acrylate oligomer, 37.6% hexane diol diacrylate, 3% phenyl benzophenone, and 3% methyl diethanol amine.

25. A method as claimed in claim 13, 15 or 21 wherein, said coating comprises, by weight, 61% of a 60/40 mixture of epoxy acrylate oligomer and hexane diol diacrylate, respectively, 32% TiO_2, 3% Trigonal 12 and 4% acyl phosphene oxide.

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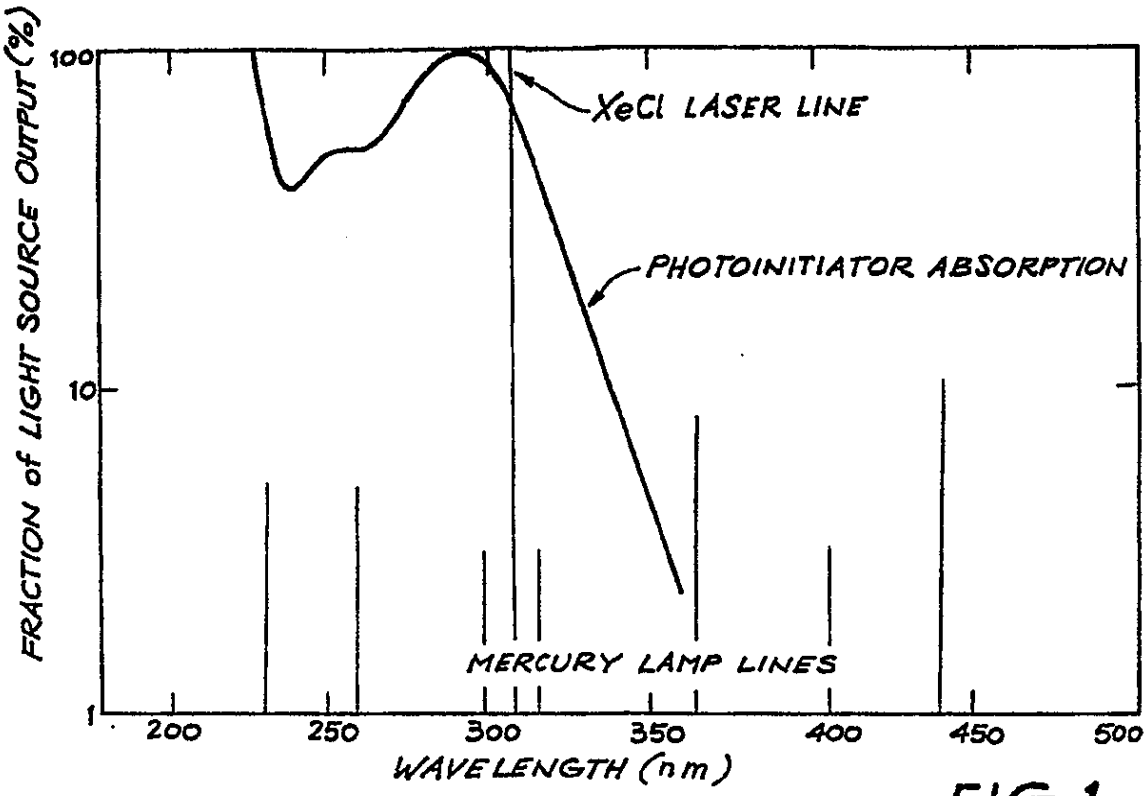
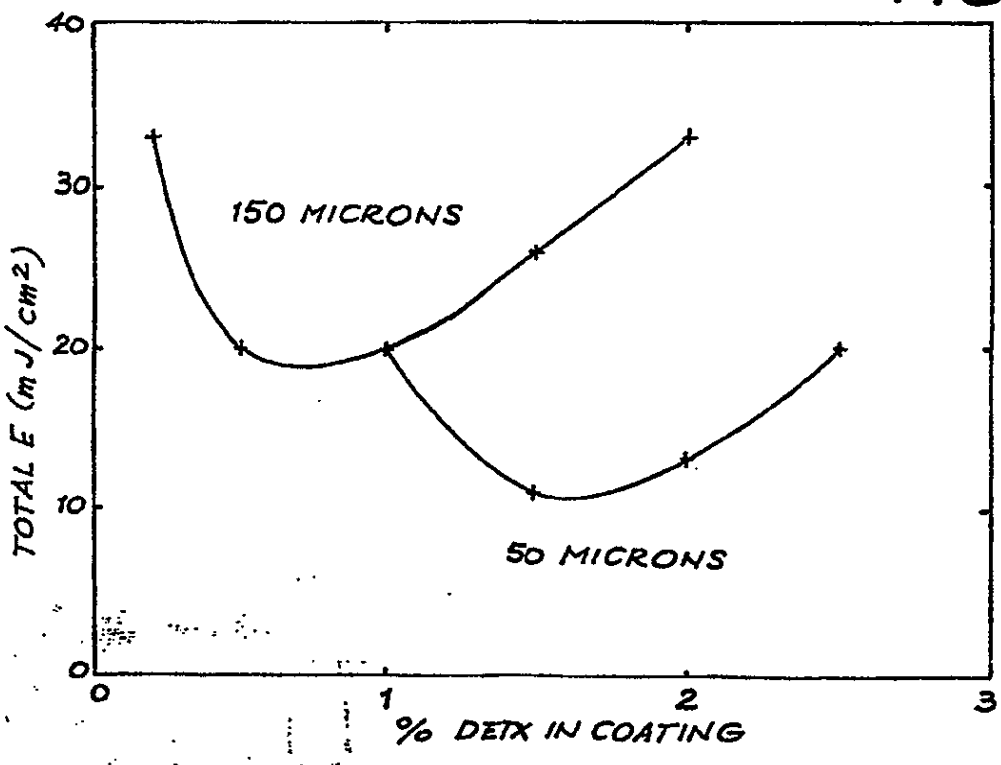


FIG. 1

FIG. 2



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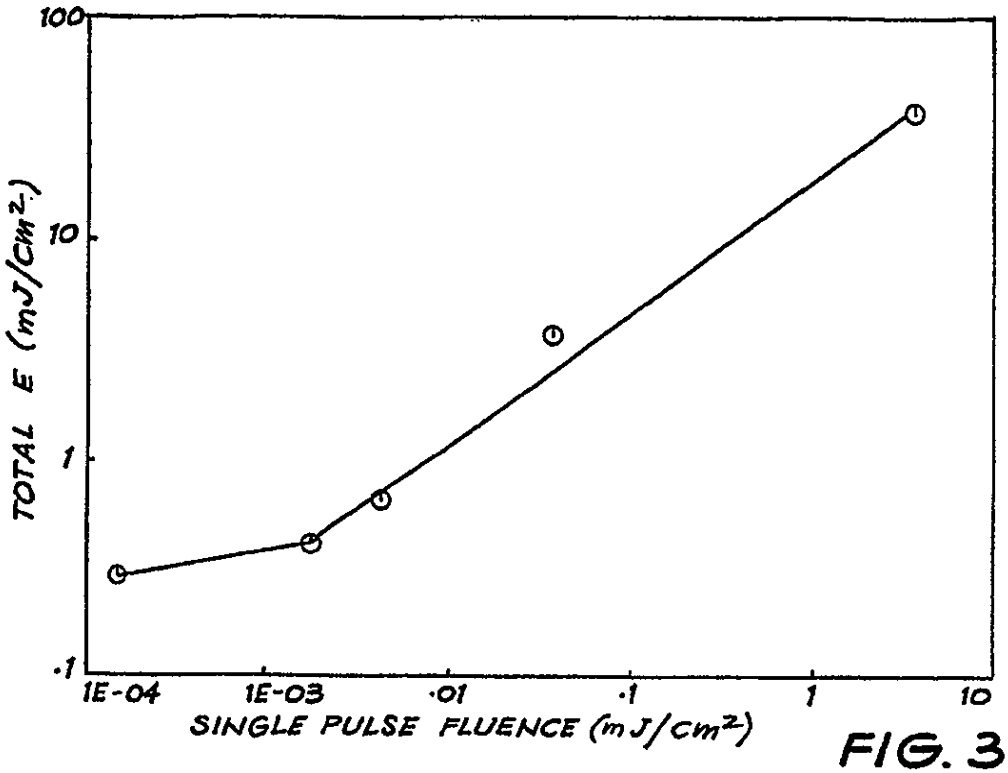
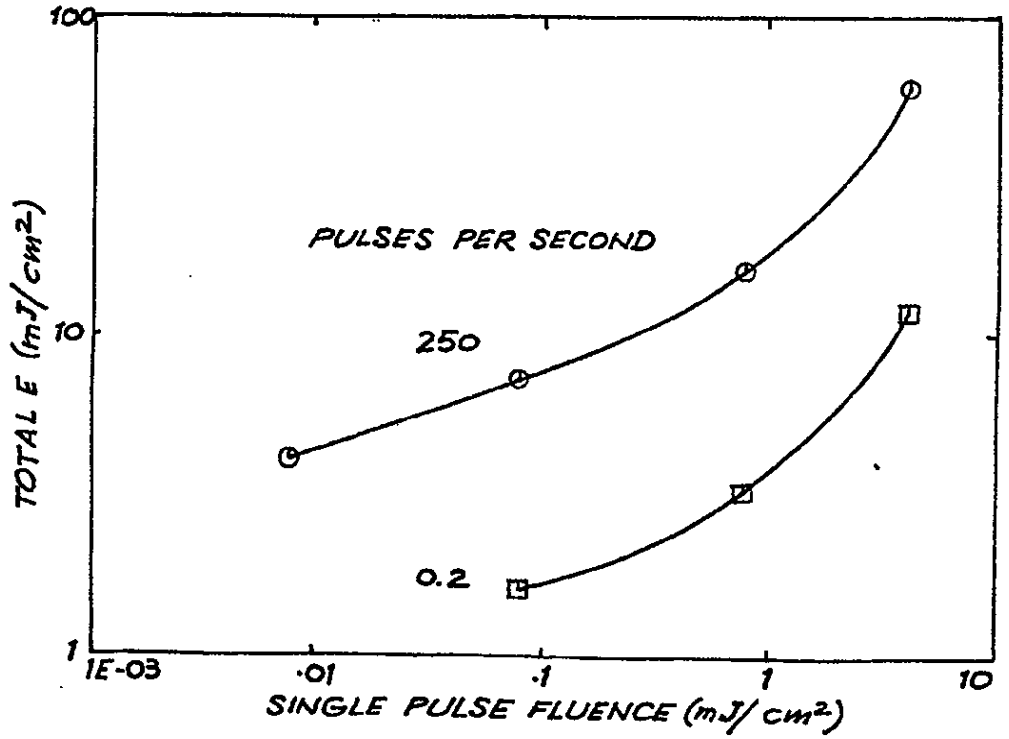

100
10
1
.1
TOTAL E (mJ/cm²)
1E-04
1E-03
·01
·1
1
10
SINGLE PULSE FLUENCE (mJ/cm²)

FIG. 3

FIG. 4


100
10
1
TOTAL E (mJ/cm²)
PULSES PER SECOND
250
0.2
1E-03
·01
·1
1
10
SINGLE PULSE FLUENCE (mJ/cm²)

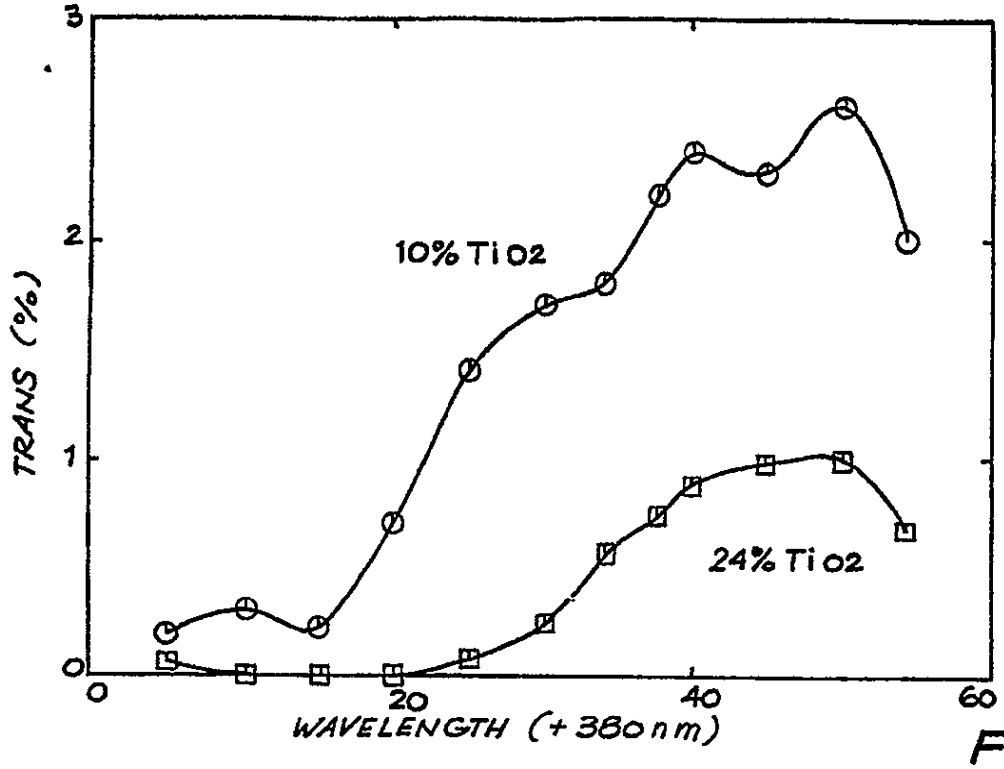


FIG.5

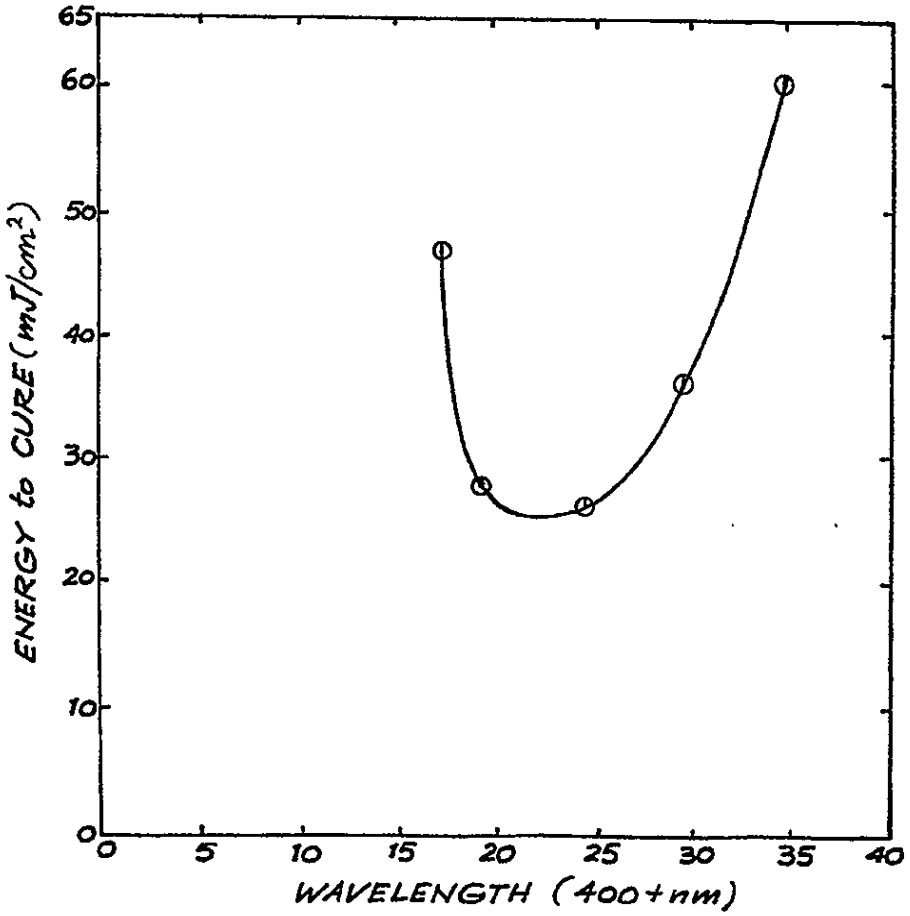


FIG.6

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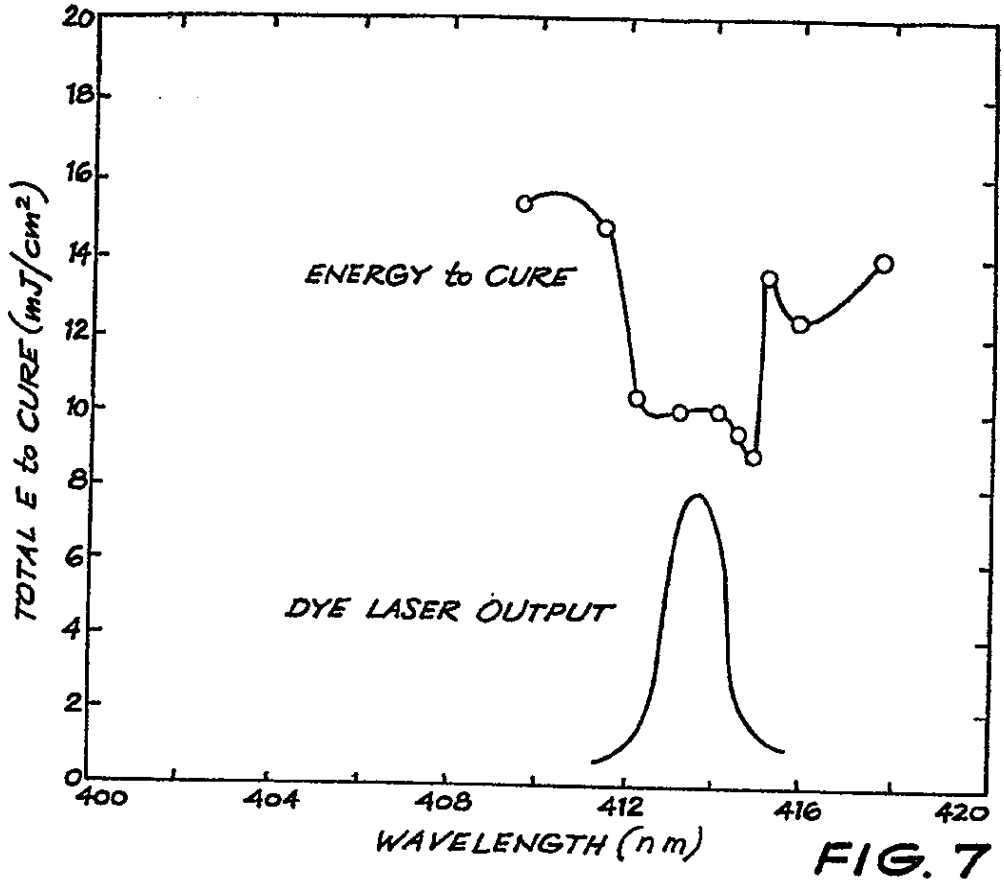

FIG. 7

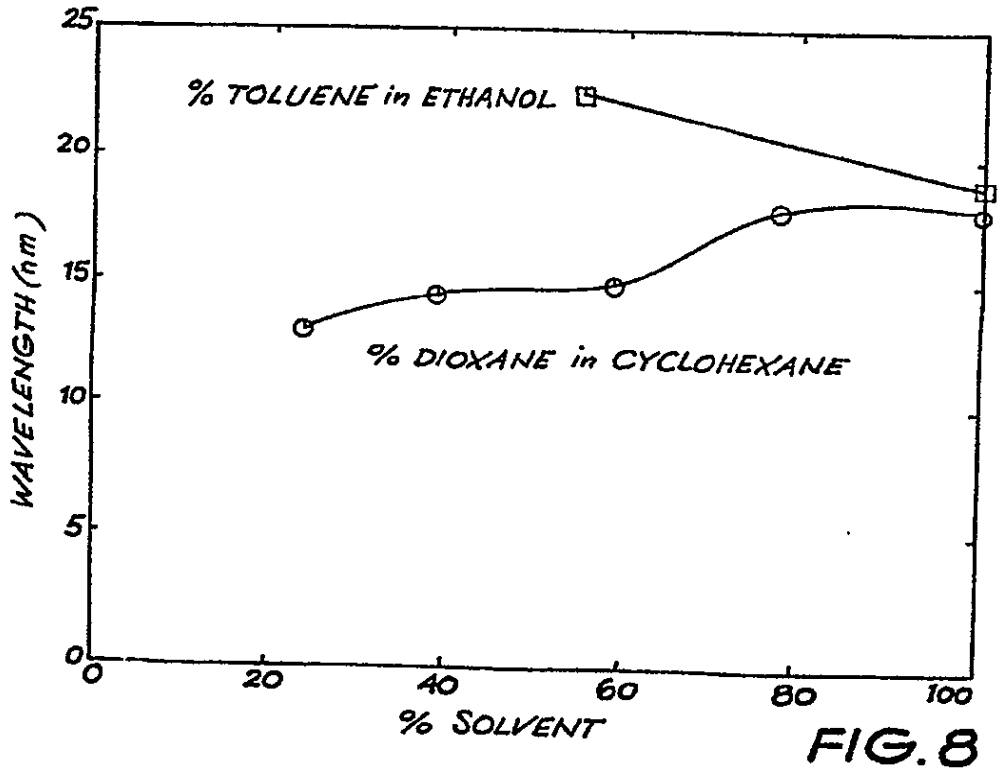

FIG. 8

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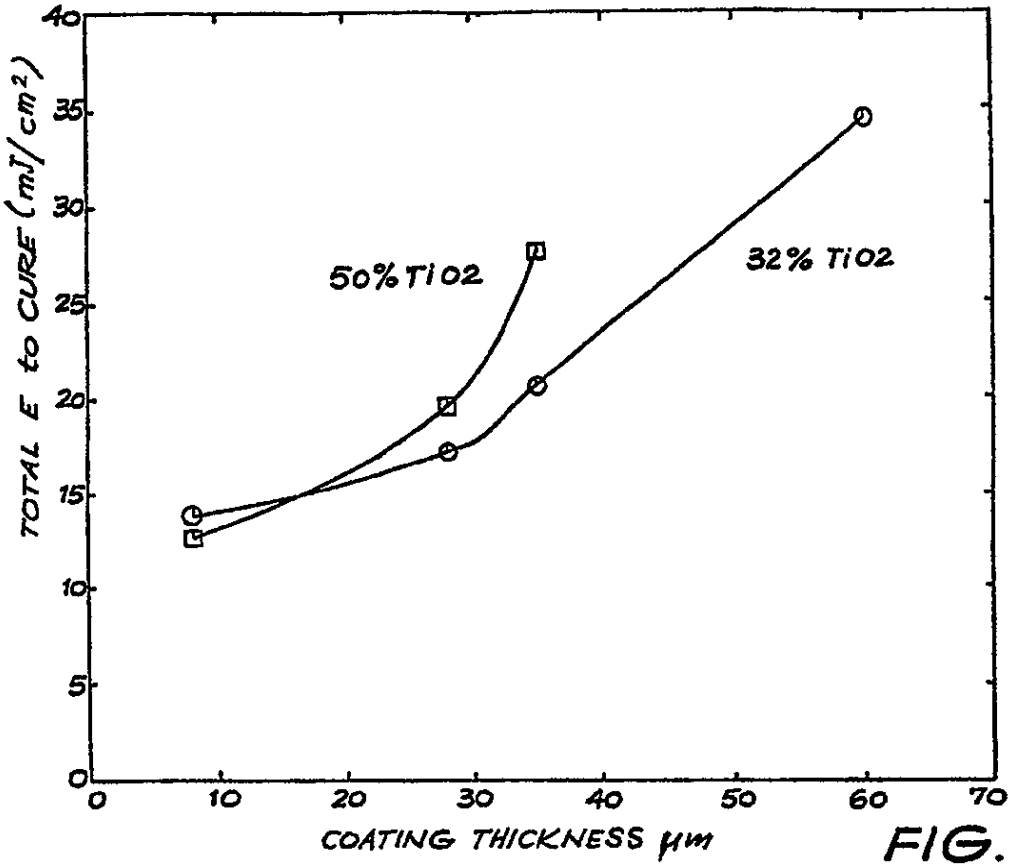
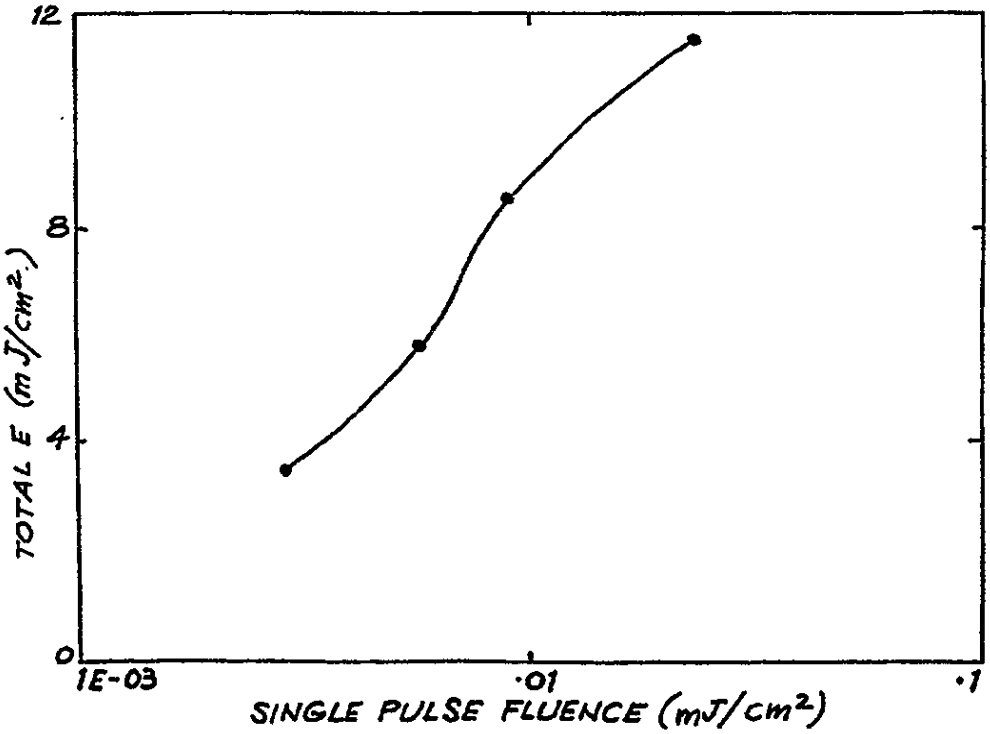


FIG. 9

FIG. 10



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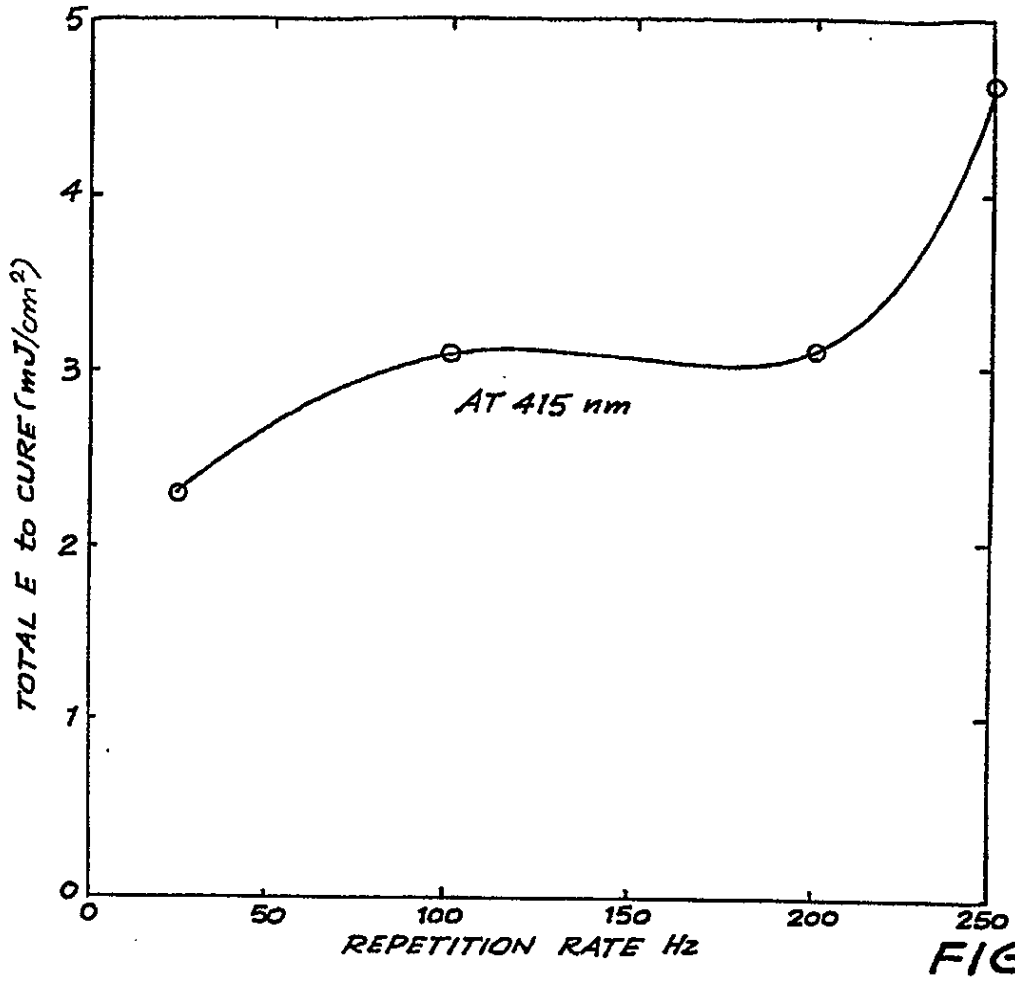
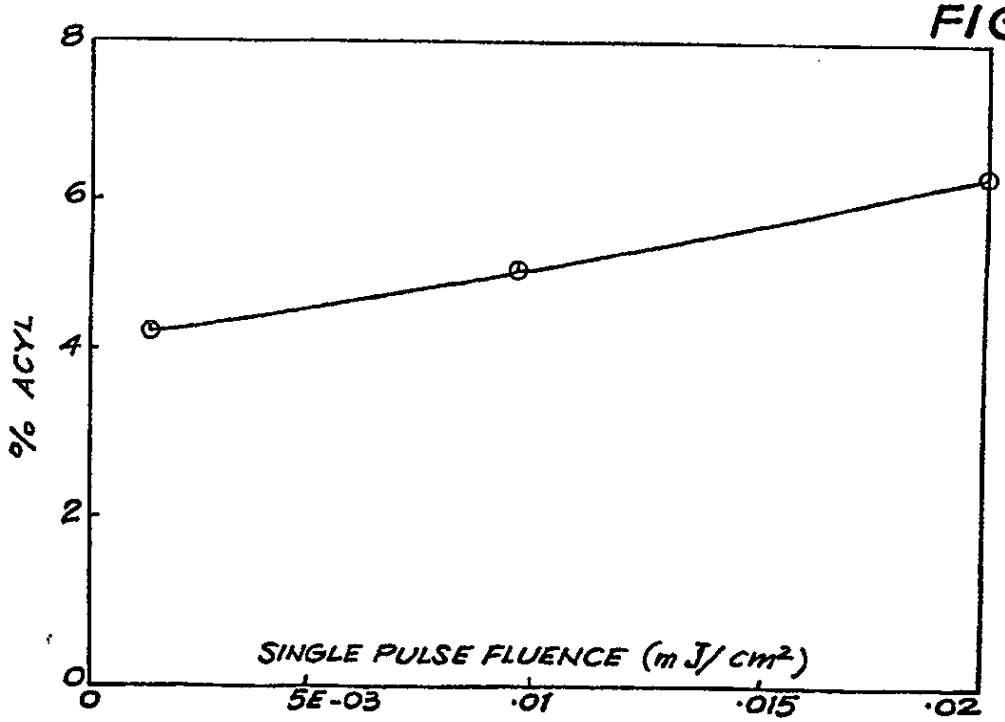


FIG. 11

FIG. 12



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